Theoretical calculation of eutectic temperature and composition in iron–carbon base ternary and multicomponent alloys

AKIO KAGAWA, TAIRA OKAMOTO
The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567, Japan

Changes in the stable and metastable eutectic temperatures and compositions of the iron–carbon system by addition of alloying elements were calculated on the basis of the geometrical thermodynamics. The influences of alloying elements on these temperatures and compositions exhibit periodicities. The periodicities of the influences on the stable and metastable eutectic temperatures have a maximum in raising these temperatures, and the periodicities of the influences on the eutectic compositions have a maximum in lowering them, in each periodic row. The calculation of eutectic temperatures was extended to Fe–C base multicomponent alloys, and the calculated eutectic temperatures were in good agreement with experimental ones given by Oldfield.

1. Introduction

For a theoretical approach to the solidification phenomena of cast irons, it is of fundamental importance to know the eutectic temperature and composition in the multicomponent systems. In earlier work [1, 2], the authors have presented the relationship between the effect of alloying elements on the eutectic temperature and the coefficient for partition of the elements during eutectic solidification. In the present work, factors influencing the eutectic temperature and composition were researched and the periodicities of the influences of alloying elements were discussed. The calculation of eutectic temperature was applied to cast irons containing various alloying elements.

2. Calculation of eutectic temperatures and compositions in Fe–C base ternary systems

In Fig. 1, a schematic diagram of the eutectic portion of the phase diagrams for the Fe–C binary and Fe–C–X ternary systems is illustrated. Changes in the stable and metastable eutectic temperatures with a third element are represented as a function of the coefficients for partition of the element during eutectic solidification, P_X^S and P_X^M, respectively [2]; for the stable system

$$\Delta T_E^S = 19.8(P_X^S - 1) \quad K\,(\text{at}\,\%\,X)^{-1} \quad (1)$$

and for the metastable system

$$\Delta T_E^M = 18.3(P_X^M - 1) \quad K\,(\text{at}\,\%\,X)^{-1} \quad (2)$$

where ΔT_E^S and ΔT_E^M are changes in the stable and metastable eutectic temperatures, respectively, with an addition of a third element of 1 at % and a positive sign of these values means increases in T_E^S and T_E^M; P_X^S and P_X^M are defined as the ratios of the atomic fraction of the element in eutectic solid to that in eutectic

liquid. In a similar way to the introduction of ΔT_E^S and ΔT_E^M, changes in carbon concentrations of the points E and A (Fig. 1) with an addition of the third element of 1 at %, ΔN_E^S and ΔN_A^S, respectively, are given by the following equations: for the stable system

$$\Delta N_E^S = 0.247\,\Delta N_C^{L(A)} + 0.753\,\Delta N_C^{L(G)} \quad (3)$$

$$\Delta N_A^S = 0.0203\,\Delta T_E^S + \Delta N_C^{A(L)} \quad (4)$$

and for the metastable system

$$\Delta N_E^M = 0.633\,\Delta N_C^{L(A)} + 0.367\,\Delta N_C^{L(C)} \quad (5)$$

$$\Delta N_A^M = 0.0203\,\Delta T_E^M + \Delta N_C^{A(L)} \quad (6)$$

where, when the values of ΔN_E^S, ΔN_A^S, ΔN_E^M and ΔN_A^M take positive signs, N_E^S, N_A^S, N_E^M and N_A^M increase; $\Delta N_C^{z(\beta)}$ (at % C/at % X) denotes a change in carbon concentration on the phase boundary of an α phase equilibrating with a β phase with an addition of the third element of 1 at %. The changes in carbon concentrations on the phase boundaries are given as follows [1]:

$$\Delta N_C^{L(A)} = \left[\frac{(P_X^{A/L} - P_{Fe}^{A/L})N_{Fe}^L}{1 - P_C^{A/L}} - \varepsilon_C^{X,L} N_C^L \right] \bigg/ (1 + N_C^L \varepsilon_C^{C,L}) \quad (7)$$

$$\Delta N_C^{L(G)} = -\varepsilon_C^{X,L} N_C^L / (1 + N_C^L \varepsilon_C^{C,L}) \quad (8)$$

$$\Delta N_C^{L(C)} = \left[\frac{(P_X^{C/L} - P_{Fe}^{C/L})N_{Fe}^L}{1 - P_C^{C/L}} - \varepsilon_C^{X,L} N_C^L \right] \bigg/ (1 + N_C^L \varepsilon_C^{C,L}) \quad (9)$$

$$\Delta N_C^{A(L)} = \left[\frac{(1/P_X^{A/L} - 1/P_{Fe}^{A/L})N_{Fe}^A}{1 - 1/P_C^{A/L}} - \varepsilon_C^{X,A} N_C^A \right] P_X^{A/L} / (1 + N_C^A \varepsilon_C^{C,A}) \quad (10)$$
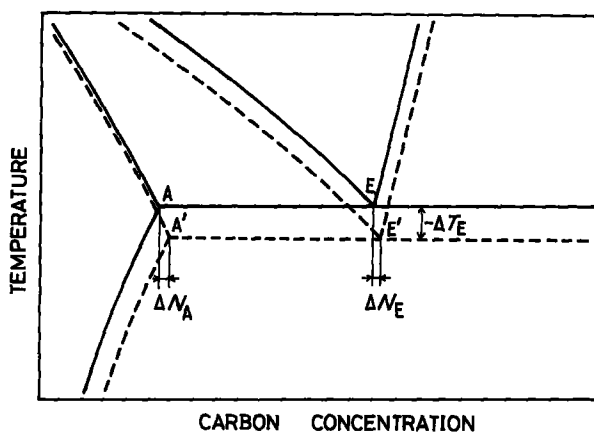
Figure 1 Schematic diagram of the eutectic portion of the phase diagrams for (——) Fe–C and (–––) Fe–C–X systems.

where $P_i^{v/L}$ is the coefficient for partition of the element i between v phase and liquid iron, being defined by the ratio of the atomic fraction of the element i in a v phase to that in liquid iron, and superscripts A, L, and C denote austenite, liquid iron and cementite, respectively; N_i^v is the mole fraction of the element i in a v phase, and $\varepsilon_i^{j,v}$ is the interaction coefficient between the elements i and j in a v phase. The values of $P_{Fe}^{v/L}$, $P_C^{v/L}$,

N_C^L and N_C^A in the Fe–C–X ternary system are approximated by those in the Fe–C binary system, when the concentration of the third element X is within a few per cent. Substituting these values in Equations 7 to 10 with those for the Fe–C binary system [3], Equations 3 to 6 are rewritten

$$\Delta N_E^S = 0.182(P_X^S - 1) - 0.067\varepsilon_C^{X,L} \qquad (11)$$

$$\Delta N_A^S = 0.167(P_X^S - 1) - 0.052\varepsilon_C^{X,A} P_X^{A/L} \qquad (12)$$

$$\Delta N_E^M = 0.221(P_X^S - 1) + 0.508(P_X^S - P_X^M)$$
$$- 0.067\varepsilon_C^{X,L} \qquad (13)$$

$$\Delta N_A^M = 0.196(P_X^S - 1) + 0.372(P_X^S - P_X^M)$$
$$- 0.052\varepsilon_C^{X,A} P_X^{A/L} \qquad (14)$$

where

$$P_X^S = P_X^{A/L} f_A^S \qquad (15)$$

$$P_X^M = P_X^{A/L} f_A^M + P_X^{C/L}(1 - f_A^M)$$
$$= [f_A^M + (1 - f_A^M)P_X^{C/A}]P_X^{A/L} \qquad (16)$$

and f_A^S and f_A^M are the mole fractions of austenite in the stable and metastable eutectic, respectively. The values of $\varepsilon_C^{X,L}$, P_X^S and P_X^M for various alloying elements are listed in Table I.

TABLE I Interaction coefficients and partition coefficients during eutectic solidification for various alloying elements.

Atomic number	Element X	$\varepsilon_C^{X,L}$ at 1426 K*	$\varepsilon_X^{X,L}$ at 1426 K	P_X^S	P_X^M†
1	H	4.94	0	0.66	—
5	B	11.70	—	0.12	0.15
6	C	15.33	15.33	1	1
7	N	15.85	0	1.86	2.09
8	O	−7.46	−17.08	0.014	(≃0)
12	Mg	6.70	—	0.14	—
13	Al	7.68	6.96	1.34	0.55
14	Si	14.15	13.41	1.64	0.78
15	P	16.02	—	0.26	0.11
16	S	13.11	−4.86	0.067	—
21	Sc	(−40)‡	—	0.0001	(≃0)
22	Ti	−23.70	8.66	0.041	0.07
23	V	−12.41	6.63	0.11	1.20
24	Cr	−6.30	−0.99	0.50	1.32
25	Mn	−3.98	−0.74	0.67	0.90
26	Fe	—	—	1	1
27	Co	2.49	—	1.14	0.86
28	Ni	4.54	−0.01	1.37	0.90
29	Cu	7.32	−7.22	1.42	0.78
30	Zn	(10)‡	—	1.26	—
31	Ga	13.06	—	0.93	—
33	As	16.60	—	0.62	—
40	Zr	−52.50	8.66	0.0002	(≃0)
41	Nb	−17.95	4.20	0.04	—
42	Mo	−7.47	0	0.32	0.52
43	Tc	(−4)‡	—	0.84	—
44	Ru	—	—	1.26	—
45	Rh	(4)‡	—	1.24	—
46	Pd	(7)‡	—	1.07	—
47	Ag	(10)‡	−13.92	0.94	—
48	Cd	(12)‡	—	0.79	—
49	In	14.78	—	0.50	—
50	Sn	16.50	−2.71	0.38	—
51	Sb	17.90	—	0.34	—
52	Te	17.17	—	0.29	—

*Extrapolated from the values of $\varepsilon_C^{X,L}$ at 1873 K [4–7].
†From Kagawa and Okamoto [8] (the values in parentheses are estimated).
‡The values of $\varepsilon_C^{X,L}$ in parentheses are estimated from the periodicity shown in Fig. 3.
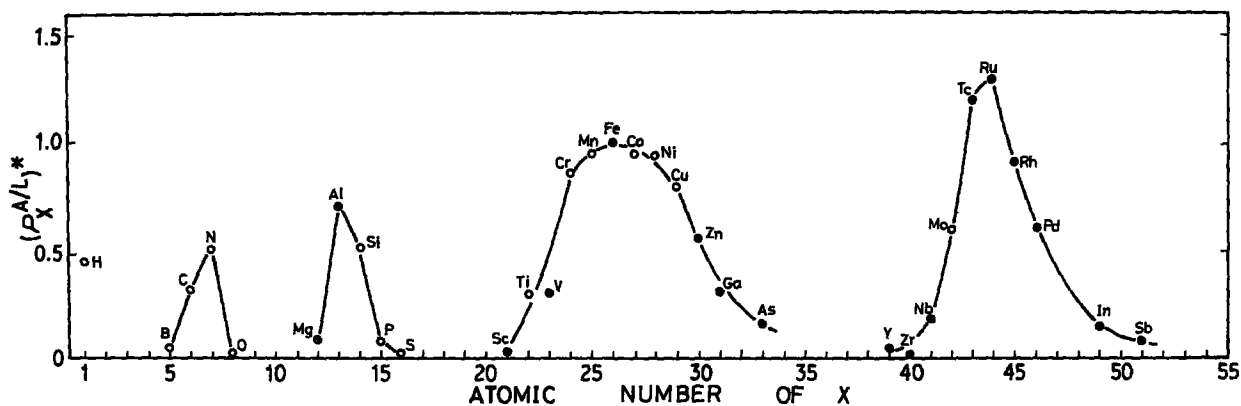
Figure 2 Periodicity of the partition coefficient of an alloying element between austenite and liquid iron in the Fe–X binary system. (O) Sims [13] Chipman [22]; (●) Kubaschewski [14]; (◐) Okamoto *et al.* [9].

3. Periodicity of the influence of alloying elements on the eutectic temperature and composition

The coefficient for partition of an alloying element X between austenite and liquid iron is related to the interaction coefficient through the following equation [8]:

$$P_X^{A/L} = (P_X^{A/L})^* \exp (\varepsilon_X^{C,L} N_C^L - \varepsilon_X^{C,A} N_C^A)$$
$$\simeq (P_X^{A/L})^* \exp (\varepsilon_X^{C,L}) \quad (17)$$

where

$$C = (1 - 0.925 P_C^{A/L}) N_C^L$$

and [23]

$$\varepsilon_X^{C,A} = 0.925 \varepsilon_X^{C,L} \quad (18)$$

where $(P_X^{A/L})^*$ is the coefficient for partition of the element X between austenite and liquid iron in the Fe–X binary system, and C is a constant for a dilute solution of the element X. The periodicity of the interaction coefficient between carbon and element X in liquid iron at about 1800 K has been established by

some workers [10–12]. Both the partition coefficient, $(P_X^{A/L})^*$, and the interaction coefficient, $\varepsilon_C^{X,L}$, extrapolated to 1426 K exhibit different periodicities as shown in Figs 2 and 3. The former has a maximum in each periodic row. As shown in Figs 4 and 5, P_X^S and ΔT_E^S have similar periodicities to $(P_X^{A/L})^*$ through Equations 1 and 15, respectively. The periodicities of ΔN_E^S and ΔN_A^S result from those of P_X^S, $\varepsilon_C^{X,L}$ and $P_X^{A/L}$ through Equations 11 and 12 and become more complex as shown in Fig. 6, where the periodic curves of the first and second periodic rows (short periodic rows) are different from those for the third and fourth periodic rows (long periodic rows).

For the metastable system, the calculation of P_X^M is limited by the lack of thermochemical data concerning cementite, and hence the partition coefficients are evaluated from Equation 16 for some elements for which the partition coefficient between cementite and austenite is known experimentally. Periodicities of P_X^M and ΔT_E^M in Figs 7 and 8, respectively, show maxima similar to the cases of P_X^S and ΔT_E^S, and those of ΔN_E^M and ΔN_A^M in Fig. 9 are complex like those for the stable system.
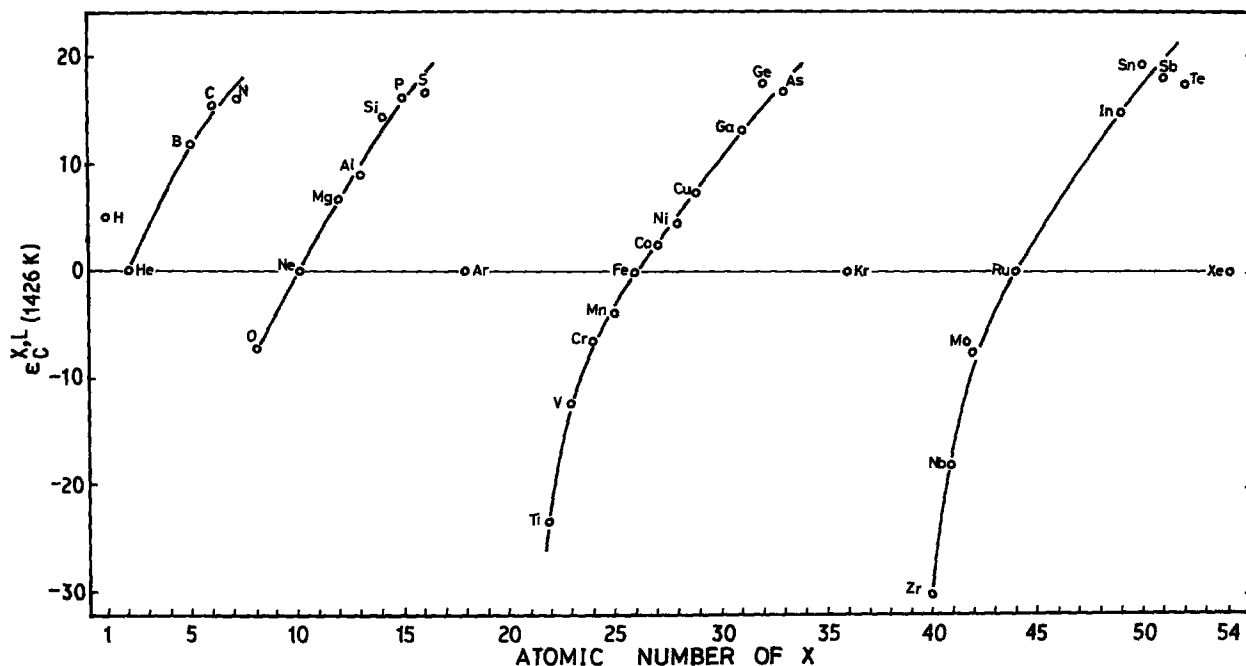

Figure 3 Periodicity of the interaction coefficient between carbon and Element X in liquid iron.
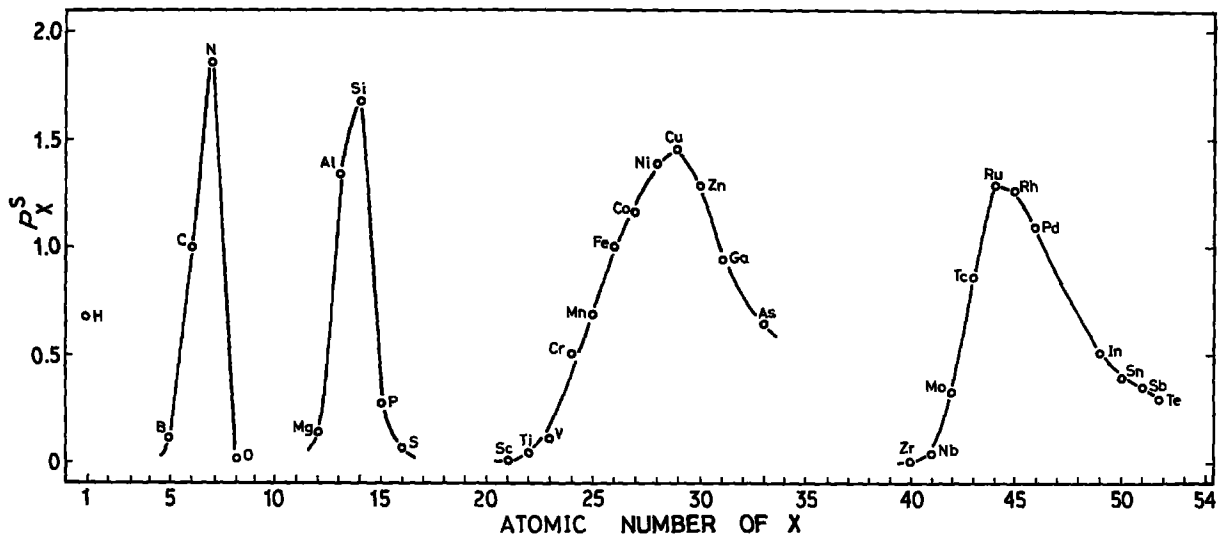
645

Figure 4 Periodicity of the partition coefficient of an alloying element during stable eutectic solidification.

In Figs 5 and 8, the increase in the stable and metastable eutectic temperatures by an addition of an alloying element has an upper limit in each periodic row. From Equations 1 and 2, lower limits of ΔT_E^S and ΔT_E^M exist for the elements having the partition coefficients $P_X^S = 0$ and $P_X^M = 0$, respectively. The elements giving upper limits of ΔT_E^S and ΔT_E^M are located in the middle of the periodic rows, while those giving the lower limits are situated at both edges of the periodic rows. On the other hand, in the periodicities of ΔN_E^S and ΔN_A^S as well as ΔN_E^M and ΔN_A^M, the elements giving minima in the periodic curves belong to the families of IIIA, IVA and VA elements and the elements located at the beginning of the third and fourth periodic rows have a marked effect to increase N_E^S and N_E^M.

4. The stable and metastable eutectic temperatures of iron–carbon base multicomponent alloys

The constants in the right-hand sides of Equations 1 and 2 are given by the following equations, respectively:

$$C_1 = \frac{27.06(1 - N_E^S P_C^{A/L})}{(1 + N_E^S \varepsilon_C^{C,L})(1 - P_C^{A/L})} \tag{19}$$

$$C_2 = \frac{13.26 P_C^{A/L}(1 - N_E^M)(1 - P_C^{C/L}/P_C^{A/L})}{(1 + N_E^S \varepsilon_C^{C,L})(1 - P_C^{A/L})(1 - P_C^{C/L})} \tag{20}$$

where $C_1 = \Delta T_E^S/(P_X^S - 1)$, $C_2 = \Delta T_E^M/(P_X^M - 1)$. The dependences of these constants on the concentration of an alloying element are involved in the values of N_E^S, N_E^M and $P_C^{A/L}$. The value of $P_C^{C/L}$ can be regarded as constant for the elements substituting iron .
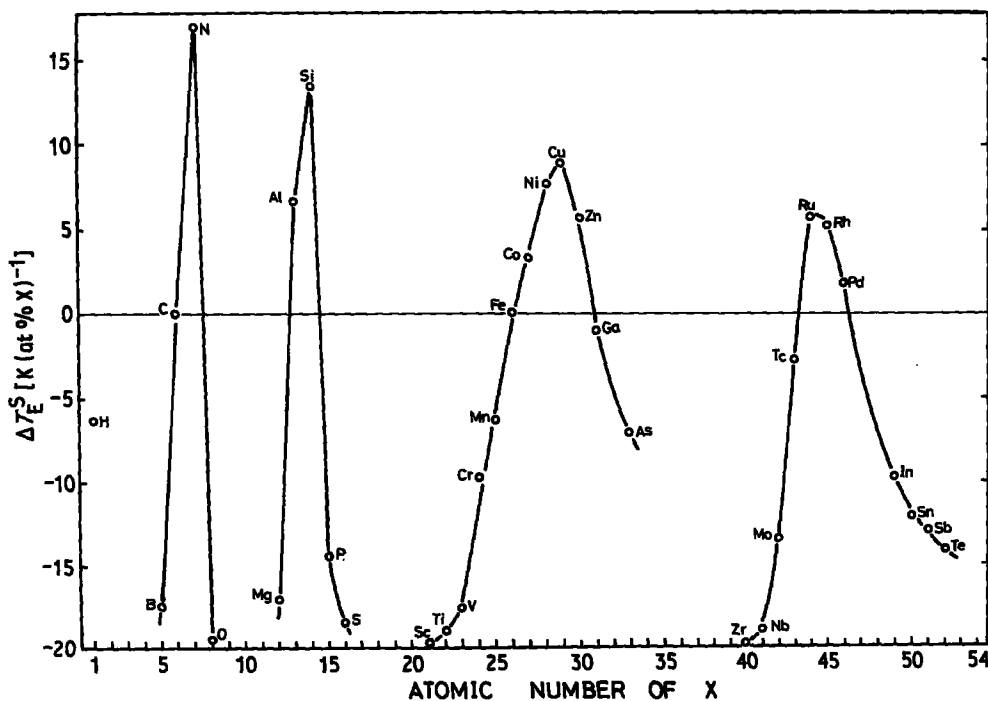

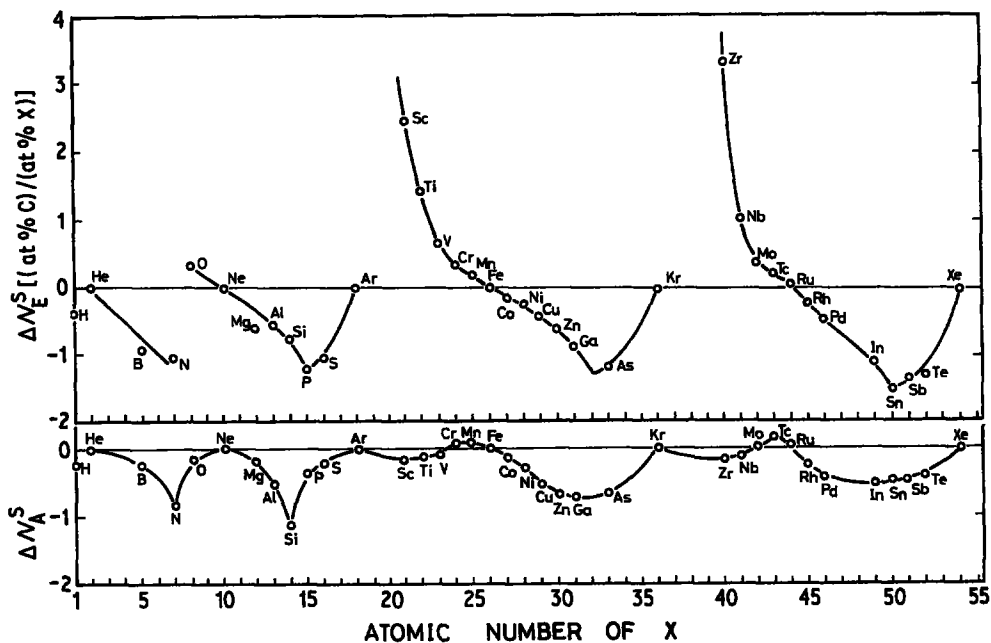*Figure 5* Periodicity of the influence of an alloying element on the stable eutectic temperature.

Figure 6 Periodicities of the influences of an alloying element on the carbon concentrations at Points E and A in Fig. 1 for the stable system.

in cementite. The dependences of ΔT_E^S and ΔT_E^M on the concentration of alloying elements are, therefore, evaluated by considering the concentration dependence of $P_C^{A/L}$, N_E^S, N_E^M, P_X^S and P_X^M. The calculated eutectic temperatures for Fe–C–Si and Fe–C–Cr ternary systems are illustrated in Figs 10 and 11, respectively, together with experimental values obtained by Oldfield [15, 16] and Kishitake et al. [17, 18]. The solid curves in the figures show the eutectic temperatures which were calculated by taking into account the dependences on the concentration of alloying elements, and the broken lines are those calculated regardless of the concentration dependence. There is a considerable difference between the solid and broken curves for the stable eutectic temperatures of the Fe–C–Si system, which is attributable to the noticeable dependence of P_{Si}^S on silicon concentration [19], while the solid and broken curves in the Fe–C–Cr system exhibit a small difference because of negligible dependences of P_{Cr}^S and P_{Cr}^M as well as $P_C^{C/L}$, N_E^S, and N_E^M on chromium

concentration [20]. The dependence of P_X^S on the concentration of an alloying element X is estimated from the self-interaction coefficient $\varepsilon_X^{X,L}$, given in Table I. The concentration dependence of P_X^S for the Fe–C–Si system is mainly due to a large interaction between silicon atoms in the solutions, while that for the Fe–C–Cr system is small because of a small interaction between chromium atoms. The calculated eutectic temperatures (solid curves) are in good agreement with the experimental ones given by Kishitake et al. [17, 18] who used the pure Fe–C–Si and Fe–C–Cr alloys in their experiments, while the eutectic temperatures obtained by Oldfield [15, 16] are lower than the calculated ones except the stable eutectic temperature for the Fe–C–Cr system. The specimens used in the experiments of Oldfield were from industrial cast irons and contained various impurity elements. The effects of these elements on the eutectic temperatures may not be negligible. The eutectic temperatures calculated for an Fe–C–Si–Mn–Cr–Ti–S
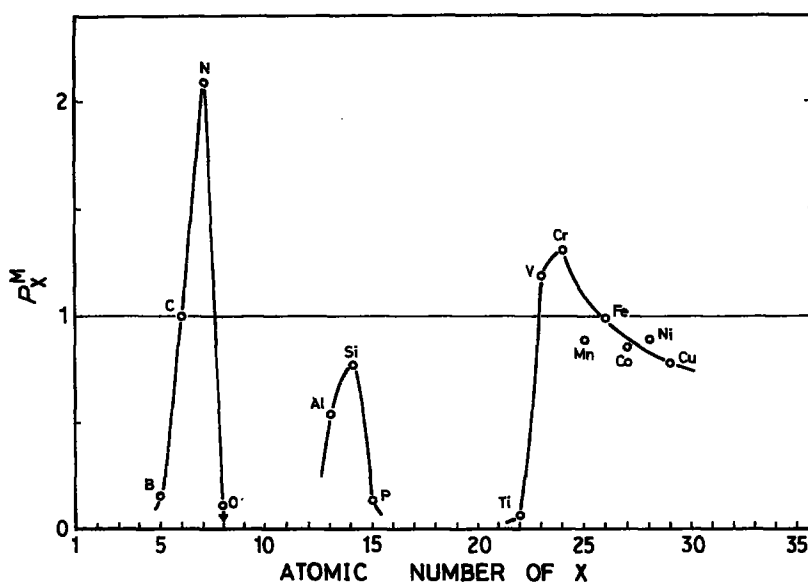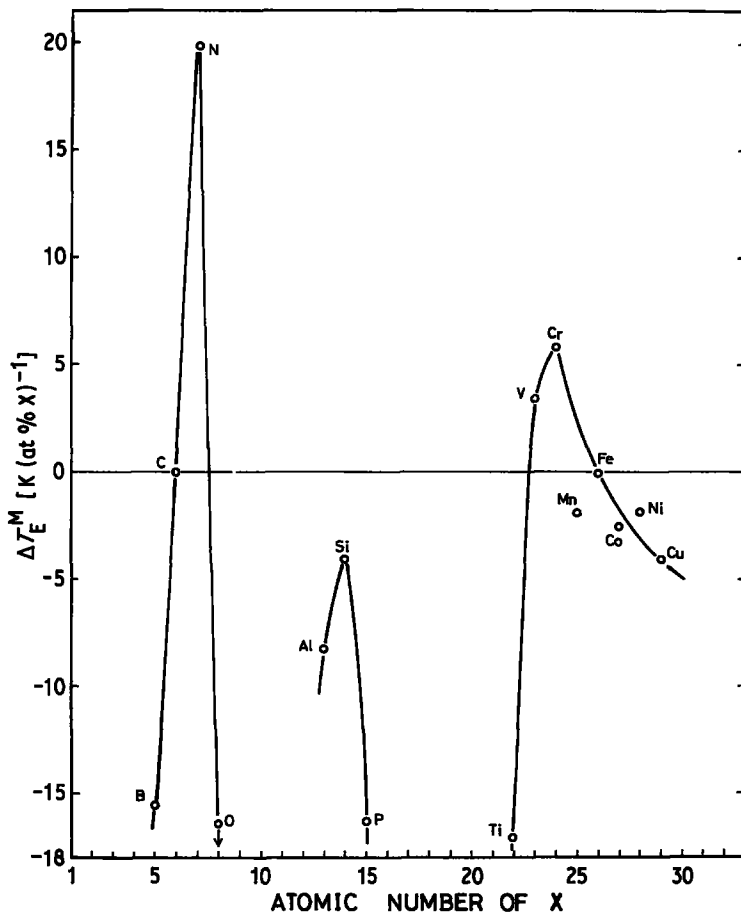

Figure 7 Periodicity of the partition coefficient of an alloying element during metastable eutectic solidification.

647

Figure 8 Periodicity of the influence of an alloying element on the metastable eutectic temperature.

system and an Fe–C–Cr–Si–Mn–Ti–S system are given in Figs 12 and 13, respectively. The concentrations of alloying elements in these systems correspond to those of the specimens used in Oldfield's experiments. In the calculation of the eutectic temperature for these Fe–C base multicomponent systems, the effects of interactions between the elements except carbon, silicon, and chromium are neglected, when the elements are on impurity levels [21]. The calculated eutectic temperatures for both the stable and metastable systems agree well with the experimental ones, except the experimental values for lower chromium concentrations in the Fe–C–Cr metastable system in

Fig. 13. This discrepancy in a low chromium concentration range may result from a low accuracy of experimental values resulting from limited data points. These results disclose the advantages of the thermodynamic calculation in determining the eutectic temperatures and compositions of cast irons without experiment.

5. Conclusions

The influences of alloying elements on the stable and metastable eutectic temperatures and compositions of the iron–carbon system were evaluated thermodynamically. The periodicities of the influences of alloying
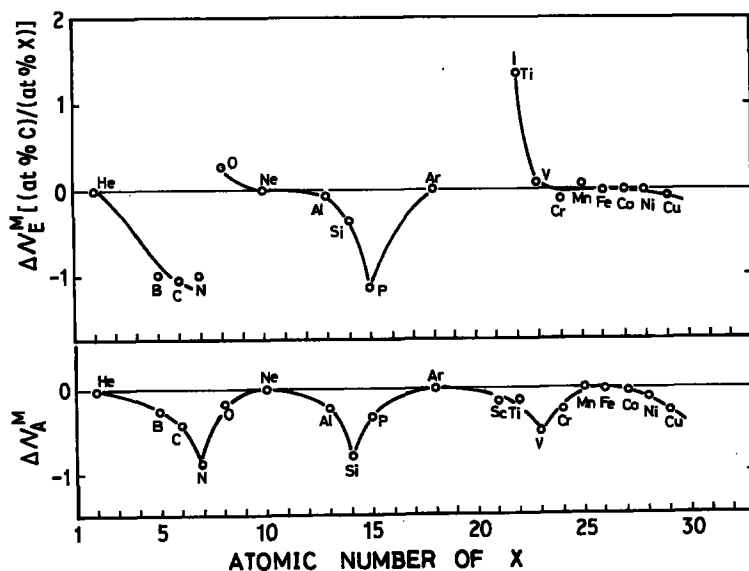

Figure 9 Periodicities of the influences of an alloying element on the carbon concentrations at Points E and A in Fig. 1 for the metastable system.
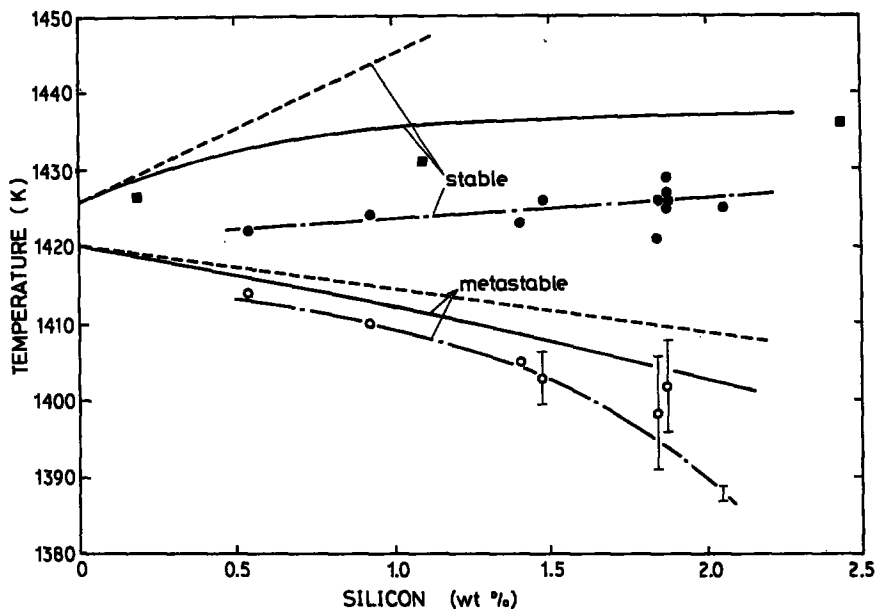
648

Figure 10 Variations in the stable and metastable eutectic temperatures of Fe–C–Si alloys with silicon concentration. (●, ○) Oldfield [16]; (■) Kishitake *et al.* [17]; (———) calculated, concentration-dependent; (– – –) calculated, no dependence.

Figure 11 Variations in the stable and metastable eutectic temperatures of Fe–C–Cr alloys with chromium concentration. (●, ○) Oldfield [15]; (■) Kishitake *et al.* [18]; (———) calculated, concentration-dependent; (– – –) calculated, no dependence.
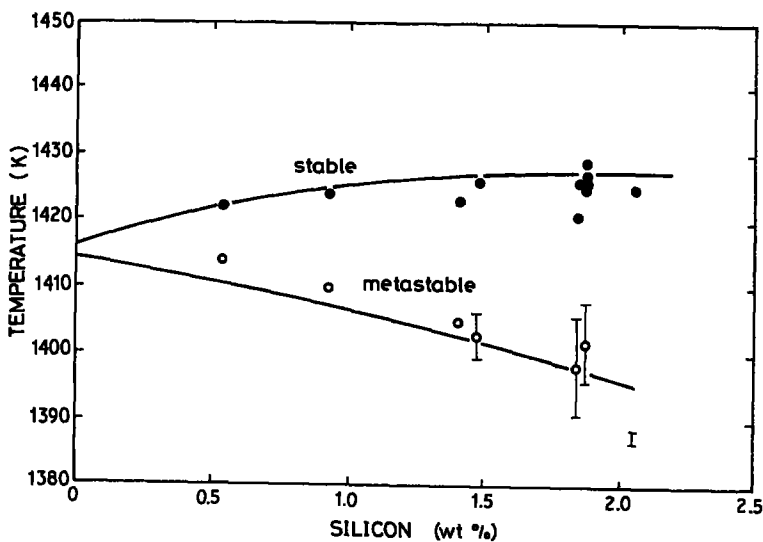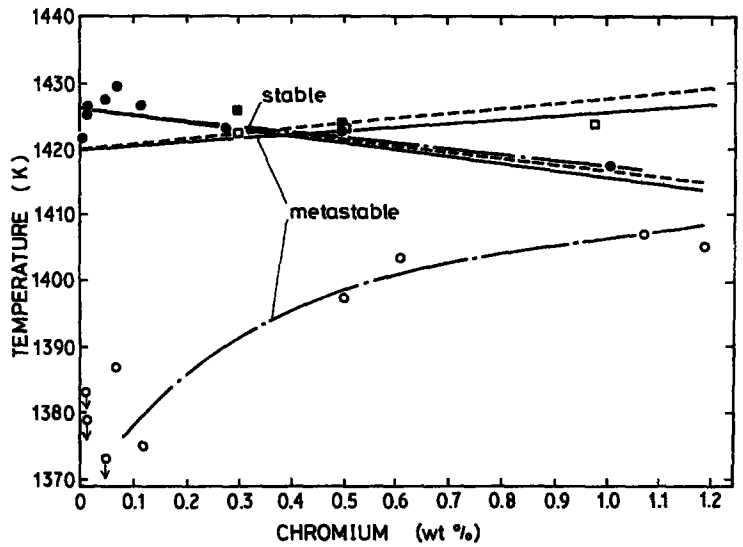

Figure 12 The stable and metastable eutectic temperatures calculated for Fe–C–Si–0.5 wt % Mn–0.1 wt % Cr–0.17 wt % Ti–0.1 wt % S alloys with the compositions equivalent to those of the specimens used in Oldfield's experiment. (———) calculated: (●, ○) Oldfield [16].
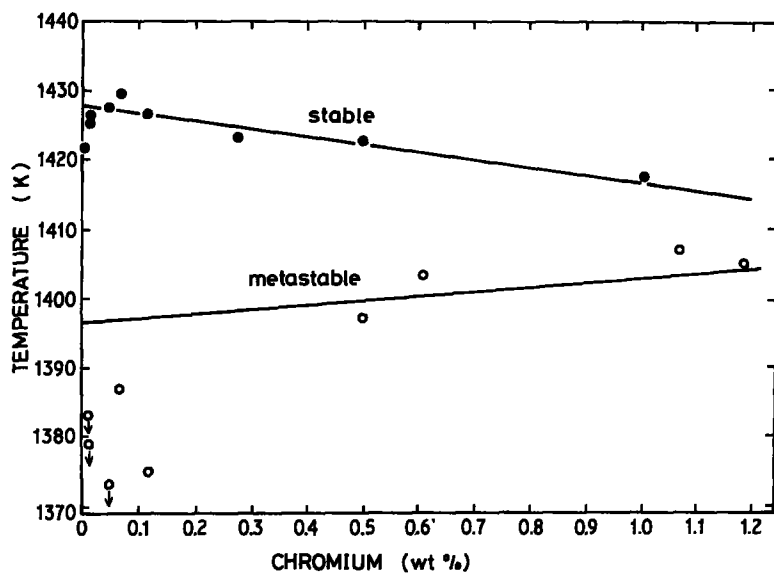
649

Figure 13 The stable and metastable eutectic temperatures calculated for Fe–C–Cr–1.9 wt % Si–0.5 wt % Mn–0.17 wt % Ti–0.1 wt % S alloys with the compositions equivalent to those of the specimens used in the Oldfield's experiment. (——) calculated; (●, ○) Oldfield [15].

elements on the eutectic temperatures and compositions were researched, and it was found that those in the stable system reflected the periodicities of the coefficient for partition of Element X between austenite and liquid iron in the Fe–X binary system, and of the interaction coefficient between carbon and Element X in liquid iron. As for the influences of alloying elements on the stable and metastable eutectic temperatures, the elements located in the middle of each periodic row show a maximum effect in raising the temperatures and those located at both edges of each periodic row show a maximum one in lowering them. The periodicities of the influences of alloying elements on the stable and metastable eutectic compositions have a maximum in lowering them in each periodic row, and the periodic curves for the first and second periodic rows differ from those for the third and fourth periodic rows.

The calculated eutectic temperatures of industrial cast irons agreed well with the experimental ones, indicating the advantages of the thermodynamic calculation for the eutectic temperatures and compositions of the Fe–C base multicomponent alloys.

References

1. A. KAGAWA and T. OKAMOTO, "The Physical Metallurgy of Cast Iron", edited by H. Fredriksson and M. Hillert (Elsevier, Amsterdam, 1985) p. 201.
2. *Idem, Imono* 57 (1985) 113.
3. M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 354.
4. G. K. SIGWORTH and J. F. ELLIOTT, *Met. Sci.* 8 (1974) 298.
5. E. SCHÜRMANN and H. RIMKUS, *Giessereiforsch.* 27 (1975) 19.
6. J. F. ELLIOTT and M. GLEISEN, "Thermochemistry for steelmaking", Vol. II (AIME and Addison-Wesley, Massachusetts, 1960) p. 564.
7. A. KAGAWA and T. OKAMOTO, *Trans. Jpn Inst. Met.* 22 (1981) 137.
8. *Idem, J. Mater. Sci.* 19 (1984) 2306.
9. T. OKAMOTO, X. HUANG and A. KAGAWA, *Met. Sci.* 18 (1984) 169.
10. F. NEUMANN and H. SCHENCK, *Arch. Eisenhüttenw.* 30 (1959) 477.
11. K. SANBONGI, M. OHTANI and K. TOITA, *Tohoku Daigaku Senkoseiren Kenkyusho Iho* 12 (1957) 97.
12. T. FUWA and J. CHIPMAN, *Trans. Met. Soc. AIME* 215 (1959) 708.
13. C. E. SIMS, "Electric Furnace Steelmaking", Vol. 2 (Wiley, New York, 1962) p. 99.
14. O. KUBASCHEWSKI, "Iron-Binary phase diagrams" (Springer, New York, 1982) pp. 5–178.
15. W. OLDFIELD, *BCIRA J.* 9 (1961) 506.
16. *Idem, ibid.* 10 (1962) 17.
17. K. KISHITAKE, T. OWADANO and K. MIYAMOTO, *Imono* 53 (1981) 295.
18. *Idem, ibid.* 53 (1981) 363.
19. A. KAGAWA and T. OKAMOTO, *Met. Sci.* 14 (1980) 519.
20. A. KAGAWA, S. MORIYAMA and T. OKAMOTO, *J. Mater. Sci.* 17 (1982) 135.
21. A. KAGAWA, K. IWATA, A. A. NOFAL and T. OKAMOTO, *Mater. Sci. Techn.* 1 (1985) 678.
22. J. CHIPMAN, "Basic Open Hearth Steelmaking" (AIME, New York, 1951) p. 632.
23. Z. MORITA and T. TANAKA, *Trans. Iron Steel Inst. Jpn* 23 (1983) 824.